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CONTINUOUS ANALYSIS IN CHEMICAL PROCESS PLANTS

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ABSTRACT

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Continuous analyzers for industrial chemical operations are reviewed and systematized. Some of the general considerations pertaining to analyzers, including the problems of coordinating them with other industrial chemical instruments and automation, are discussed. It is stressed that more knowledge of physical measurement principles than chemical processes is required, but synthesis of both is essential.

Guidelines for deciding on the most suitable method of measurement and analysis, instrumentation, maintenance procedure, etc. are presented, and various aspects of sampling the chemical product for analysis are discussed.



1. INTRODUCTION

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The objective of the chemical plant is to increase production output without lowering the required standard of quality. Modern plants have been designed on a larger scale and their instrumentation has progressed accordingly. The general trend is for the chemical plant to use advanced computerized methods of process analysis and control systems. For this reason, the development of continuous analyzers capable of working in conjunction with these techniques and systems has become indispensable.

Numbers in the margin indicate pagination in the original foreign text.

In operating continuous analyzers, it is important to know more than just that which is required in handling general industrial instruments (for example, thermometers, flowmeters, pressure gages, etc.), in other words it is essential to have a combination of chemical knowledge and the techniques of physical measurements in particular. Since, in principle, the continuous analyzer is a sort of automated analyzer on a laboratory scale, indicating and recording quantitative results, it would appear that a general knowledge of instrument analysis is sufficient to operate it. Furthermore, in view of the analytical technique involved, it would also seem to be merely a method for the quantitative analysis of known compounds. From the standpoint of the engineer in charge of measurement and process control, however, certain difficulties are encountered, which can only be overcome by extensive knowledge and adequate experience, in other words there are still problems inherent in the analyzer itself (for example, its capacity, construction, maintenance, etc.) and it must be used in coordination with other industrial instruments for processing.

Due to limited space, the present paper deals only with the general aspects of continuous analysis, omitting any detailed discussion of practical problems.

2. CONTINUOUS ANALYZERS AND THEIR CHARACTERISTICS

Table 1 lists the major continuous analyzer currently in use in chemical plants. The following are sometimes used in addition to those shown in the table: i) refractometers; ii) dielectric meters; iii) gas chromatographs with a hydrogen flame ion detector; iv) mass spectrometers; v) polarographs; vi) ultra-violet spectrophotometers; vii) neutron-optical hydroscopes. In certain special cases, analyses can also be carried out by combining some of the common industrial meters (for example, thermometer and pressure gage, etc.).

As indicated in table 1, the methods of analysis are more typically physical than chemical. This is because the actual need of the plant is simply to measure the values of certain known components automatically rather than manually, but not to detect some unknown substances or carry out qualitative analysis. The continuous analyzer must indicate quantitative data, on which the results of analysis of the controlled process can be based.

3. REMARKS ON THE PERFORMANCE OF CONTINUOUS ANALYSIS

When it is decided that an analyzer should be installed, a careful study must be made to ascertain: i) whether the function of the analyzer really meets specifications; ii) how the data gathered by the analyzer will affect processing in the plant. Otherwise, the analyzer may prove later to be of little gain.

3.1 Choice of Analytical Method and Measurement

The choice of analytical method depends on what kind of physical (or chemical) property is to be measured. The key factor in selecting the method is not only the object itself, but the perturbation of coexisting substances must also be taken into consideration.

Even within a given single analytical method, there will be two or more different systems of measurement; for example, either a detector based on thermal conductivity or a hydrogen-flame ion detector can be used as the detector in gas chromatography. In selecting the proper system, the performance, as well as the theoretical specifications, of commercial meters must be taken into account. 1711

3.2 Selection of the Analyzer

In addition to the usual considerations of instrument performance (such as its range of measurement, precision, etc.) and market price, special attention must also be devoted to the following points in picking out the analyzer:

TABLE 1						
	Analyzer	Principle of Measurement	Frequency of Usage	Process Analyzed	Characteristics	Remarks
1.	Gas densitometer	Rotary force of fan by wind pressure	☉	Mixture of two gases	Easy to operate	Uses displacement of liquid level meter
2.	Gas densitometer	Speed of sound in acoustic line	○	Mixture of two gases		
3.	Liquid hydro-meter	Level of float	☉	Flowing liquid	Sampling not required	Uses manometer
4.	Liquid hydro-meter	Surface tension by air jet	☉	Nonvolatile liquid		Caution for radioactivity
5.	Liquid hydro-meter	γ-ray absorption	○	Liquid in high pressure container	The instrument does not contact with the liquid	
6.	Thermal conductometer	Change in electrical resistance of wire by heat conduction	☉	Mixture of two gases		Widely used for many analyzers as detector
7.	Magnetic Oxygen analyzer	Attractive force of magnetism to O ₂	○		Selective for O ₂	(Model F-3 by Beckman Co.) For high or low concentration
8.	Magnetic Oxygen analyzer	Change in electrical resistance of hot wire by magnetic flux	☉	Mainly waste gas in pipe	Selective for O ₂	Special attention to a gas that changes its thermal conductivity
9.	Viscometer	Level of a float in an upward flowing liquid	○	High-polymer liquid or oil	Narrow measurable range	

TABLE 1 (Cont.)						
	Analyzer	Principle of Measurement	Frequency of Usage	Process Analyzed	Characteristics	Remarks
10.	Gas chromatograph	Thermal conductivity	⊙	Hydrocarbon gas	Many components can be measured simultaneously	Needs complex control program
11.	Colorimeter	Absorption of visible light with photo tube	○	Liquids in general	Trace components can be measured with aid of coloring reagents	Turbidometer, which measures air pollution, has same principle.
12.	Infrared spectro-photometer	Nondispersive	○	Gas in general	Has good selectivity, micro detection is possible	Quality of water can be measured by the same principle.
13.	Electro-Conductometer	Electric conductivity between two electrodes in liquid	⊙	Aqueous solution having electric conductivity		
14.	Electro-Conductometer	Electromagnetic induction	○	Aqueous solution having electric conductivity	Can be applied for corrosive liquid	
15.	pH meter	Glass electrode	⊙	Aqueous solution in general		
16.	Oxygen micro analyzer	Galvanic cell method	○	O ₂ in gas (of order of ppm.)		
17.	Hygrometer	Electric conductivity of hygroscopic substances such as LiCl or P ₂ O ₅	○	Water in gas (of order of ppm to percent)		

TABLE 1 (Cont.)					
Analyzer	Principle of Measurement	Frequency of Usage	Process Analyzed	Characteristics	Remarks
18. Explosive gas detector	Change in electrical resistance change of hot wire by heat of combustion of gas	○	Gas containing explosive gas		

Note: ◎ Very frequently

○ Average

i) Reproducibility. - Inasmuch as the plant is in twenty-four hour continuous operation, the relative values of the analyzer in comparison with two or more instruments are often more important than the absolute value. Accordingly, the rating of an analyzer should be based on its reproducibility (i.e., the extent to which it reads the same value at constant concentration of the component). Among analyzers for laboratory use are some which require repeated null-point adjustment for each new measurement. Any instrument of this type, unless changed over to automatic, is not suited to continuous analysis.

ii) Countermeasures for external perturbations. - Investigations should be made to determine the best way to correct for 1) those disturbances which are inevitable in the course of continuous analysis (caused, for example, by a perturbing component in the sample material, or a change in temperature, pressure, or flow velocity); 2) mechanical disturbances which directly affect the function of the instrument (for example, temporal fluctuations in the line voltage).

iii) Adaptability of the construction of the instrument to the operational site. - Needless to say, once installed, the instrument should function for a long period of time at the site. Consequently, the following points must be thoroughly checked prior to installation, to be sure the instrument has good endurance to:

- a) exposure to corrosive or explosive gases;
- b) shock and vibration;
- c) exposure to rain and/or wind;
- d) careless and rough handling;

iv) Ease of calibration and maintenance.

3.3 Maintenance

The maintenance of the analyzer is extremely difficult, compared with ordinary industrial instruments. It requires constant attention and intensive care not only in the inspection and testing of every part, but in adjustment of the sampling system, regular replacement of standard samples, etc.

In order to maintain the precision of the analyzer and ensure its operation at maximum power, all simple inspection should be done by the operator himself. In this way, the operator can always depend on the value indicated by the analyzer. Furthermore, he should always check the precision of the analyzer readings by comparing them with other process data.

The maintenance engineer must have broad and advanced knowledge of physics and chemistry, and he must be an expert troubleshooter on the analyzer, as it is his responsibility to inspect and calibrate the instrument at the request of the operator.

Judging from the operational data of analyzers in many plants, it appears that careful attention is exercised in the installation and test period. Once in regular operation, however, there tends to be a gradually diminishing confidence in the precision of the analyzer until, in some cases, the instrument has been abandoned due to: i) lack of adequate care in maintaining its precision or ii) incomplete investigation to locate the cause of abnormal or anomalous behavior (sometimes caused by changes in the composition or nature of the sample, or changes in operating conditions themselves). This is understandable, when one realizes that, in general, only half of the instruments currently installed are operated in a satisfactory manner.

4. SAMPLING SYSTEM

The design of the sampling system (the scheme for picking out samples from the process for input to the analyzer) is equally as important as the analyzer itself. Inadequately designed, the sampling procedure can sometimes cause inaccurate results. The design varies with the state of the sample (gas., liquid, or solid) and depends on the nature of the respective component. Confining ourselves to the case of a fluid sample, the factors deserving special attention are as shown in table 2.

TABLE 2	
Samples not well mixed	Extract sample portions from several outlets and mix.
Gas flowing in line	Take sample from upper outlet; sediment may be accumulated in lower section.
Sludge formation	Too small an outlet causes the sample to be left inside.
Gas on surface of boiling water	Avoid contamination by splashing.
Processing of gas at high temperature	Partial condensation sometimes seen at outlet; maintain constant temperature.
Processing of liquid at low temperature	Fluid flow rate tends to change due to partial evaporation at outlet; maintain constant temperature.
Processing of fluid under high pressure	Take precautions to avoid change in sample composition by condensation of gas due to adiabatic expansion or by escape of gas dissolved in liquid.
Processing of fluid in vacuum	Prevent leakage.

4.1 Proper Position of Outlet and Sampling Procedure

There are still certain problem over and above the factors shown in table 2 (for example, how to avoid changes in the sample by some chemical reaction in the sampling system).

4.2 Conduits in Sampling System

TABLE 3	
Change in material of conduit line	Select material that resists chemical or physical reaction or high temperatures.
Width and length of conduit	Smooth and rapid transport of sample (with no more than two or three minutes lag) is required; consideration must be given to the position of the detector; too narrow a line becomes clogged with dust.
Obstruction in line	Obstruction will sometimes occur in the conduit when the fluid sample is fed into single analyzer by switching from two or more processing systems; often results in analytical error

4.3 Preprocessing Equipment

1) Due to a certain component being present in the sample, the analyzer may be damaged (for example, introduction of an acidic gas into an analyzer measuring traces of O_2 in the alkaline state on the basis of the redox potential).

2) Analytical error can be produced by lowering of the selectivity due to improper components in the sample (as in the case of a wet gas being fed into an infrared gas analyzer).

3) Error may be caused by an essential disturbance of the baseline (for example, feeding an O_2 -soluble liquid into a polarograph).

Certain measures must be taken to eliminate the above-mentioned disturbances before the sample is fed into the analyzer. Table 4 shows the preprocessing chemicals commonly used for that purpose.

TABLE 4	
<u>Chemical</u>	<u>Preprocessed substances</u>
Silica gel	Water in gas
Calcium chloride	Water in gas
Activated charcoal	Organic gases and liquids
Conc. sulfuric acid	Alkaline substances and wet gases
Sodium hydroxide soln.	Sulfides and acidic substances

If any of the solid chemicals in table 4 is used, appropriate filters should be placed around the chemical in order to preclude diffusion. In the case of liquid chemicals it is important to avoid splashing when the sample goes through the liquid. It must also be taken into consideration that preprocessing may cause the concentration of the sample to vary. For example, when water is removed from a sample originally consisting of 80% N_2 , 10% CO_2 , 1712 10% H_2O , the resultant composition becomes 89% N_2 , 11% CO_2 .

4.4 Filters

Since dust and unnecessary suspensions (or particles) in the fluid sample may upset the process if the sample is delivered directly into the analyzer, filters may be used. Normally, a metal screen or a packet of glass wool is inserted in the line. Perforated stainless steel plates have also been used recently.

For the most part, two filter systems and the preprocessing system are installed in parallel, enabling the analyzer to operate continuously even during

cleaning of one filter system.

Although it is not strictly a filter, the cyclone used to separate liquid from gas is used. In the event that the measurements become disturbed by bubbles (as in the case of an electroconductometer, turbidometer, etc.), a bubble-eliminating device is used.

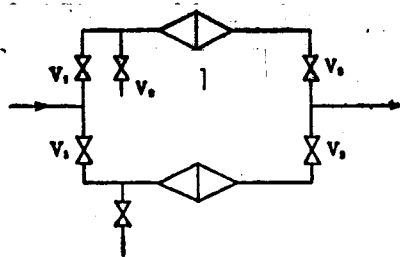


Figure 1.

Legend: 1) Filter. Note: If the process is run at high pressure or temperature, or if toxic compounds are involved, the sample can be withdrawn through V_2 , after which the filter is safely removed.

If not needed, V_2 may be omitted.

4.5 Pressure Regulator and Safety Valve

It is normally required that the pressure of the sample introduced into the analyzer be at atmospheric or slightly higher. Consequently, if the processing system is either pressurized or operates with a vacuum, the sample pressure must be adjusted to near-atmospheric prior to input. Sampling systems operating off of high-pressure processes are shown in figure 2 (a - gas; b - liquid). The pressure regulator from a pressurized gas cylinder may be used as the pressure reducing valve. The pressure reduction can be indicated on a Bourdon gage or U-tube manometer. A safety device is necessary in order to protect the analyzer against damage due to accidental over-pressures. As shown in figure 2, if the

gas pressure is increased, bubbles escape from a liquid seal (a) and the liquid overflows from a reservoir when the liquid pressure is increased (b). Should the above devices not be suitable, a safety valve must be incorporated. When the process utilizes vacuum, a pressurizing device (booster) is installed in a bypass line, as shown in figure 3, and the sample must be extracted after the adjustment to atmospheric pressure. However, if the sample gas is pressurized at the process temperature, the composition of the sample may be altered by 1713 condensation of the gas.

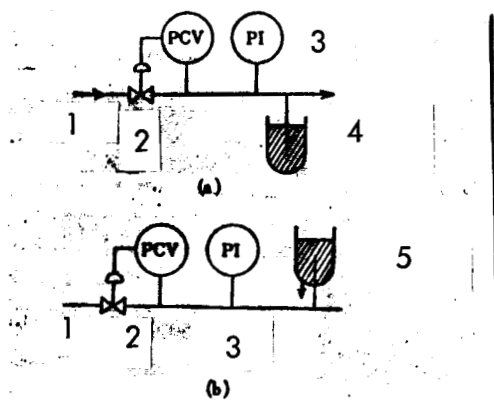


Figure 2.

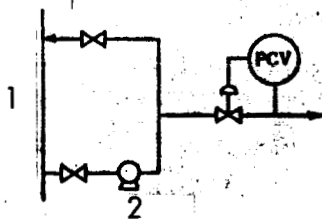


Figure 3.

Legend:

- 1) process;
- 2) pressure-reducing valve;
- 3) pressure gage;
- 4) safety trap (liquid seal);
- 5) safety trap (liquid overflow type).

Legend:

- 1) process line;
- 2) booster.

4.6 Checking the Fluid Flow System

Once the sampling system starts to operate, the sample must flow continuously. If the analyzer exhibits any abnormal indications, the sample flow should be checked at once. This means that some device must be installed to check to flow.

The sample flow is typically 200 ml/min to 2 liter/min in the case of a gas. In the case of a liquid, it depends on the type of analyzer, but the flow rate in the detector section is more or less 10 cm/sec to 1 m/sec. To observe the flow quantitatively, either a rotameter or U-tube manometer should be used. Quantitative measurement, however, is not always essential, in a number of instances simple confirmation of the flow is enough. In the case of a liquid, the flow can be observed through an illuminated window installed in a downstream position. The rotameter is adequate in the case of gases.

4.7 Sampling Outlet for Chemical Analysis

As a check on the function of the analyzer, the sample taken from the sampling system should be analyzed in the laboratory and the values compared with those read on the analyzer. The difference between the laboratory-analytical results and the analyzer readings does not necessarily indicate a trouble situation in the function of the instrument. It may be a matter of what part of the sampling system the sample is taken from.

The sample exit point for laboratory analysis should be installed in the conduit line of the sampling system. In any case, taking into account the process characteristics, careful attention should be devoted to the time at which the test sample is withdrawn. Otherwise, correct sampling may be impossible due to condensation of gas or the adsorption of some substance to the container.

4.8 Insertion of the Standard Sample

In order to maintain and check the null point and full scale adjustment of the analyzer, standard samples are prepared and preserved in tight cylinders. From time to time, these standard samples are introduced into the analyzer in place of the operating sample (this operation must be simple and straightforward), and the results obtained thereby are used to calibrate the analyzer.

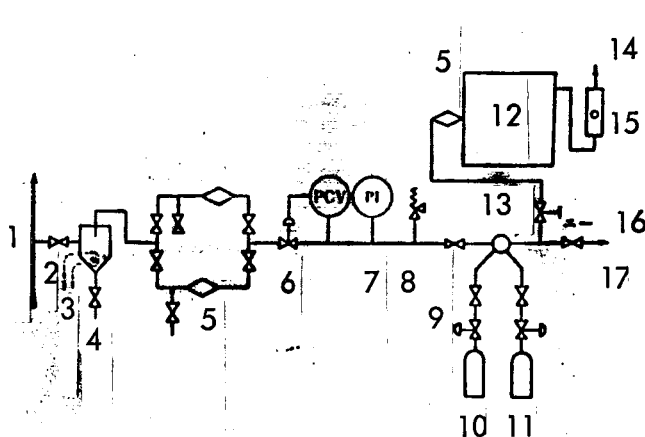


Figure 4a. Gas Sampling

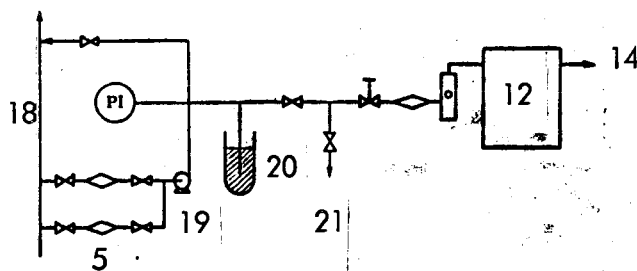


Figure 4b. Gas sampling

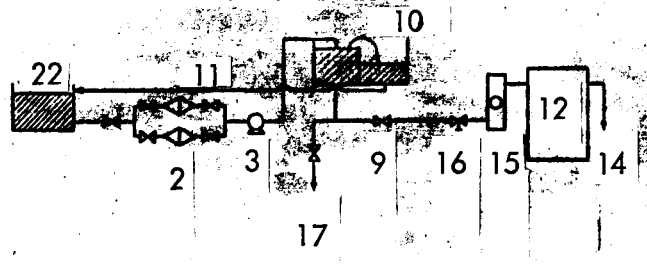


Figure 4c. Liquid Sampling

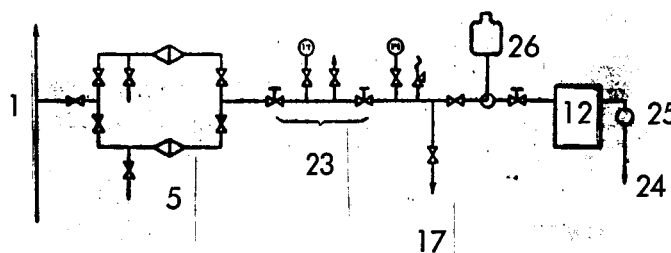


Figure 4d. Liquid sampling

Legend:

- | | |
|---|--|
| 1) process (high pressure); | 13) switching valve; |
| 2) valve; | 14) outlet; |
| 3) cooling line; | 15) rotameter; |
| 4) drain valve; | 16) needle valve; |
| 5) filter; | 17) sample outlet; |
| 6) pressure-reducing valve; | 18) process (vacuum); |
| 7) pressure gage; | 19) pump; |
| 8) safety valve; | 20) liquid seal; |
| 9) stop valve; | 21) sample outlet; standard gas inlet; |
| 10) standard gas for null-point adjustment; | 22) process; |
| 11) standard gas for full-scale adjustment; | 23) two-stage pressure reduction; |
| 12) analyzer; | 24) to low-pressure process; |
| | 25) illuminated window; |
| | 26) standard liquid. |

4.9 Conclusion

The sampling systems described above in sections 4.1 to 4.4 are shown schematically in figure 4. Although these are not always best suited to every situation, they deserve attention from the general standpoint.